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Title : A METHOD AND APPARATUS
: FOR PRODUCING A
: PLASMA DISPLAY

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CLAIM FOR PRIORITY UNDER 35 U.S.C. §119

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

We submit herewith the verified English translations of Japanese Patent Application No. HEI9-081555, filed March 31, 1997, Japanese Patent Application No. HEI8-336713, filed December 17, 1996, Japanese Patent Application No. HEI9-172364, filed June 27, 1997, Japanese Patent Application No. HEI9-172339, filed June 27, 1997, and Japanese Patent Application No. HEI9-172354, filed June 27, 1997, the priority of which is hereby claimed.

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Verification of Translation

I, Shuji Sawada of 2-34-1710, Heso 2-chome, Ritto-cho, Kurita-gun, Shiga 520-3031 JAPAN, state that

1. I am familiar with the Japanese and English languages.
2. I have read the attached translation into Japanese Patent Application No. HEI8-336713 filed on December 17, 1996 and the attached translation is a accurate translation of the Japanese-language original document.

Executed at Otsu-shi, Shiga-ken this 17th day of March, 2000.

Shuji Sawada

Shuji Sawada

**PATENT OFFICE
JAPANESE GOVERNMENT**

**This is to certify that the annexed is a true copy of the following application as filed
at this Office.**

Date of Application : December 17, 1996

Application Number : Patent Applivation No. HEI 8-336713.

Applicant(s) : Toray Industries, Inc.

**Commissioner,
Patent Office**

Toshimitsu Arai

[Title of the document] REQUEST FOR GRANT OF PATENT

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[Title of the invention] A method for producing a plasma display

[Number of claims] 10

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[Title of the document] Drawing 1

[Title of the document] Abstract 1

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[Title of the invention] A method for producing a plasma display

[Claims]

[Claim 1] A method for producing a plasma display, in which a glass substrate with partitions formed on it is coated with a fluorescent paste containing a fluorescent material and an organic binder discharged from a paste applicator with outlet holes, and the paste is burned to form a fluorescent material layer, characterized in that the spaces A between the respectively adjacent partitions and the average diameter B of the outlet holes satisfy the following condition:

$$500 \mu\text{m} \geq A > B \geq 10 \mu\text{m}$$

[Claim 2] A method for producing a plasma display, according to claim 1, wherein the fluorescent paste is discharged continuously from the outlet holes, to form a fluorescent material layer.

[Claim 3] A method for producing a plasma display, according to claim 1, wherein fluorescent material layers different in color are formed in stripes.

[Claim 4] A method for producing a plasma display, according to claim 1, wherein a fluorescent powder with an average grain size of 0.5 to 6 μm is used.

[Claim 5] A method for producing a plasma display, according to claim 4, wherein the fluorescent powder is 1 to 15 μm in the

grain size of 50 vol% of the grains and 0.1 to 2 m²/g in the specific surface area.

[Claim 6] A method for producing a plasma display, according to claim 1, wherein the fluorescent paste has the following composition.

Organic component : 15 ~ 60 parts by weight

Fluorescent powder : 40 ~ 85 parts by weight

Solvent : 10 ~ 50 parts by weight

[Claim 7] A method for producing a plasma display, according to claim 1, wherein the fluorescent paste has a viscosity of 0.1 to 100 poises.

[Claim 8] A method for producing a plasma display, according to claim 1, wherein the organic binder contains 10 wt% or more of a photosensitive compound.

[Claim 9] A method for producing a plasma display, according to claim 1, wherein the coating with the fluorescent paste is followed by a drying step, exposure step, development step and burning step, to form the fluorescent material layer.

[Claim 10] A method for producing a plasma display, according to claim 1, wherein the coating with the fluorescent powder is followed by a step of drying with the fluorescent material coated side turned downward, to form the fluorescent material layer.

[Detailed description of the invention]

[Technical field of the invention]

The present invention relates to a new method for producing a plasma display panel. The plasma display panel of the present invention can be used as a display for wall mounted television sets and information displays.

[Prior arts]

The conventionally known methods for producing plasma display panels include screen printing. Especially for forming fluorescent materials of plasma displays, screen printing has been frequently used.

Japanese Patent Laid-Open (Kokai) No. 6-5205 proposes to use sand blasting after screen printing, and Japanese Patent Laid-Open (Kokai) No. 5-144375 proposes to effect screen printing after coating with a crosslinking agent. Both the techniques use screen printing.

However, screen printing does not allow a highly precise pattern to be formed disadvantageously since the screen is deformed by repeated printing, and also in view of control such as washing of the screen, screen printing cannot be said to be suitable for mass production.

Furthermore, for obtaining a highly precise pattern, photolithography is used. However, in this case, to form the respective fluorescent material layers of red, green and blue, the respective steps of coating, exposure, development, drying, burning, etc. must be repeated three times, to raise the cost disadvantageously.

It is also proposed to eject a fluorescent paste from the tip of an ink jet nozzle, for forming a fluorescent material layer. However, in the case of ink jet, the viscosity of the fluorescent paste must be kept at 0.2 poise or less, and since the amount of the fluorescent powder in the paste cannot be increased, the thickness of the formed fluorescent material layer is too thin disadvantageously. There is another problem that since the ink jet nozzle must be smaller in diameter, it is clogged with the fluorescent powder.

[Problems to be solved by the invention]

The inventors studied intensively to find a method for producing a plasma display panel free from the above disadvantages, and as a result, the present invention has been completed. The object of the present invention is to provide a plasma display panel which allows a fluorescent material layer to be formed simply at high accuracy.

[Means for solving the problems]

The object of the present invention can be achieved by a method for producing a plasma display, in which a glass substrate with partitions formed on it is coated with a fluorescent paste containing a fluorescent material and an organic binder discharged from a paste applicator with outlet holes, and the paste is burned to form a fluorescent material layer, characterized in that the spaces A between the

respectively adjacent partitions and the average diameter B of the outlet holes satisfy the following condition:

$$500 \mu\text{m} \geq A > B \geq 10 \mu\text{m}$$

[Embodiments of the invention]

In the method of the present invention, a glass substrate 3 with electrodes 1 and partitions 2 formed on it is partially coated with a fluorescent paste, particularly florescent materials emitting light of three primary colors of red, blue and green in stripes, to form a red fluorescent material layer 4, a blue fluorescent material layer 5 and a green fluorescent material layer 6 respectively.

Since three stripes of red (R), blue (B) and green (G) form one pixel line, they must be formed in repetition of RGB or RBG.

For forming the fluorescent material layers, at first, a paste containing one fluorescent material selected from three colors of R, G and B is discharged from a paste applicator 8 with one or more outlet holes 7, for coating the substrate, and this operation is repeated three times for R, G and B. Then, the pastes are dried and burned, to form the fluorescent material layers. As another method, the respective fluorescent materials of R, G and B can be discharged from a paste applicator with outlet holes for simultaneously discharging R, G and B, dried and burned, to form the respective fluorescent material layers.

It is preferable to discharge the fluorescent pastes simultaneously from a paste applicator with 600 to 2500 outlet holes for discharging the respective colors of R, G and B, since the processing time can be shortened.

It is preferable that the inner diameter of the outlet holes used in the present invention is 10 to 500 μm , and a more preferable range is 50 to 200 μm . In this case, it is preferable that the partitions 2 are formed at a pitch of 80 μm to 500 μm , and a more preferable range is 80 to 200 μm . Furthermore, if the inner diameter B of the outlet holes is smaller than the spaces A formed between the respectively adjacent partitions, the mixing of adjacent colors can be prevented.

To discharge a fluorescent paste from outlet holes, it is preferable to press the paste continuously at a pressure in a certain range, for discharging the past by the pressure. In this case, the amount of the paste discharged can be kept constant, and a coating layer with a stable thickness can be obtained.

In the present invention, after the fluorescent paste is discharged from the outlet holes, it undergoes a drying step and a heating step such as burning step, to evaporate or decompose water, organic solvent, organic component, etc. for removing them, thereby forming a fluorescent material layer formed by a fluorescent powder only.

In this case, if the fluorescent material coated side is turned downward during heating, the fluorescent paste moves along the lateral sides of the partitions, to form a fluorescent material layer also along the lateral sides of the partitions. If the fluorescent material layer is formed not only on the spaces between the partitions but also along the lateral sides of the partitions, the fluorescent material face can have a larger area, to effectively improve the luminance of the plasma display.

If a photosensitive fluorescent paste is used as the fluorescent paste, patterning by photolithography can be applied. In this case, the fluorescent material formed on unwanted portions such as the tops of the partitions by coating can be effectively removed.

After the respective photosensitive fluorescent pastes of R, G and B colors are discharged from the outlet holes for coating, they are exposed through a photomask, so that the pastes in the exposed portions may be made soluble or insoluble in the developer, and the unnecessary portions are removed in the development step, to form the fluorescent material layers of the respective colors.

The fluorescent powders used in the present invention are not especially limited. For example, those emitting light of red include $Y_2O_3:Eu$, $YVO_4:Eu$, $(Y, Gd)BO_3:Eu$, $Y_2O_3S:Eu$, $g-Zn_3(PO_4)_2:Mn$, $(ZnCd)S:Ag+In_2O_3$, etc. Those emitting light of

green include $\text{Zn}_2\text{GeO}_4:\text{Mn}$, $\text{BaAl}_{12}\text{O}_{19}:\text{Mn}$, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{LaPO}_4:\text{Tb}$, $\text{ZnS}:\text{Cu,Al}$, $\text{ZnS}:\text{Au,Cu,Al}$, $(\text{ZnCd})\text{S}:\text{Cu,Al}$, $\text{Zn}_2\text{SiO}_4:\text{Mn,As}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}$, $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$, $\text{ZnO}:\text{Zn}$, etc. Those emitting light of blue include $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$, $\text{BaMgAl}_{14}\text{O}_{23}:\text{Eu}$, $\text{BaMgAl}_{16}\text{O}_{27}:\text{Eu}$, $\text{BaMg}_2\text{Al}_{14}\text{O}_{24}:\text{Eu}$, $\text{ZnS}:\text{Ag}+\text{red pigment}$, $\text{Y}_2\text{SiO}_5:\text{Ce}$, etc.

Furthermore, the present invention allows the use of rare earth element tantalate fluorescent materials in which at least one matrix forming rare earth element selected from yttrium (Y), gadolinium (Gd) and lutetium (Lu) is substituted by at least one element selected from a group consisting of thulium (Tm), terbium (Tb) and europium (Eu). A preferable rare earth element tantalate fluorescent material is europium activated yttrium tantalate represented by composition formula $\text{Y}_{1-x}\text{Eu}_x\text{TaO}_4$ (where x is approximately 0.005 to 0.1). A preferable red fluorescent material is europium activated yttrium tantalate, and a preferable green fluorescent material is terbium activated yttrium tantalate represented by composition formula $\text{Y}_{1-x}\text{Tb}_x\text{TaO}_4$ (where x is approximately 0.001 to 0.2). A preferable blue fluorescent material is thulium activated yttrium tantalate represented by $\text{Y}_{1-x}\text{Tb}_x\text{TaO}_4$ (where x is approximately 0.001 to 0.2).

Further preferable green fluorescent materials include a manganese activated zinc fluorescent material ($\text{Zn}_2\text{SiO}_4:\text{Mn}$) with an average grain size of 2 μm to 8 μm activated by 0.2 wt%

to less than 0.1 wt% of manganese based on the weight of zinc silicate (Zn_2SiO_4) matrix, and a manganese activated zinc silicate fluorescent material represented by general formula $(\text{Zn}_{1-x}\text{Mn}_x)\text{O} \cdot \alpha\text{SiO}_2$ (where $0.01 \leq x \leq 0.2$ and $0.5 < \alpha \leq 1.5$).

The grain size of the fluorescent powders used in the above is selected, considering the line width, inter-line space and thickness of the fluorescent material layer pattern to be prepared. However, it is preferable that the powder is 0.5 to 15 μm , especially 0.5 to 6 μm in the average grain size of 50 wt% of the grains and 0.1 to 2 m^2/g in specific surface area. It is more preferable that the grain size is 1 to 6 μm and that the specific surface area is 0.2 to 1 m^2/g . If the grain size and the specific surface area are in these ranges, a highly precise pattern can be obtained. Furthermore, the luminous efficiency of the fluorescent material can be enhanced and the life can be elongated preferably. If the powder is less than 1 μm in grain size or more than 2 m^2/g in specific surface area, the powder is so fine that in the case of patterning by photolithography, the light is scattered during exposure, to photoset the portions not exposed. As a result, the fluorescent materials remain in the non-exposed portions at the time of development, not allowing a highly precise pattern to be obtained. Furthermore, the luminous efficiency and life of the fluorescent materials decline.

As for the form of the fluorescent powder, polyhedral grains can be used, but it is preferable that the powder is not cohesive. It is more preferable that the powder is spherical grains since the influence of scattering during exposure can be lessened. It is preferable that spherical grains account for 80% or more in the fluorescent powder in the number of grains. It is more preferable that spherical grains account for 90% or more. If spherical grains account for less than 80% in number, it is difficult to obtain a highly precise pattern, because of the influence of scattering by the fluorescent powder at the time of exposure to ultraviolet light. To measure the spherical grain percentage, the fluorescent powder is photographed at 300 times by an optical microscope, and the number of countable grains is counted, to calculate the rate of spherical grains as the spherical grain percentage.

The organic component used in the present invention contains an organic binder, solvent, plasticizer and, as required, such additives as a dispersing agent and leveling agent.

The organic binders which can be used here include, for example, (poly)vinyl butyral, (poly)vinyl acetate, (poly)vinyl alcohol, cellulose polymers (e.g., methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, methylhydroxyethyl cellulose), polyethylene, silicone polymers (e.g., (poly)methylsiloxane,

(poly)methylphenylsiloxane), polystyrene, butadiene/styrene copolymer, (poly)vinylpyrrolidone, polyamides, high molecular polyesters, ethylene oxide-propylene oxide copolymer, polyacrylamide, and various acrylic polymers (e.g., sodium polyacrylate, (poly) lower alkylacrylates, (poly) lower alkylmethacrylates and various copolymers and multipolymers of lower alkylacrylates and methacrylates.

The plasticizers which can be used here include, for example, dibutyl phthalate, dioctyl phthalate, polyethylene glycol, glycerol, etc.

The solvents which can be used here include, for example, methyl cellosolve, ethyl cellosolve, butyl cellosolve, methyl ethyl ketone, dioxane, acetone, cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, tetrahydrofuran, butylcarbitol acetate, dimethyl sulfoxide, γ -butyrolactone, bromobenzene, chlorobenzene, dibromobenzene, dichlorobenzene, bromobenzoic acid, chlorobenzoic acid and organic solvent mixtures containing at least one or more of the foregoing.

In the present invention, a fluorescent material layer can also be formed by using a photosensitive fluorescent paste with an organic component containing a photosensitive compound and a fluorescent powder as essential ingredients.

It is preferable that the organic component used in the photosensitive fluorescent pastes contains 10 wt% or more of a photosensitive compound. More preferable is 25 wt% or more.

The organic component containing a photosensitive compound contains at least one photosensitive ingredient selected from photosensitive polymers, photosensitive monomers and photosensitive oligomers, and furthermore, as required, also such additives as photopolymerization initiator, sensitizer and ultraviolet light absorber.

It is preferable that the amount of the organic component containing a photosensitive compound used in the present invention is 15 to 60 wt%. If less than 15 wt%, the pattern property is degraded due to insufficient sensitivity, and if more than 60 wt%, the removal of the binder by burning is insufficient.

The photosensitive component can be either a light insolubilizable photosensitive component or a light solubilizable photosensitive component. The light insolubilizable photosensitive components which can be used here include the following:

- (1) A component which contains one or more functional monomers, oligomers and polymers with one or more unsaturated groups in the molecule
- (2) A component which contains a photosensitive compound such as an aromatic diazo compound, aromatic diazide component or organic halogen compound
- (3) A so-called diazo resin such as a condensation product of a diazo based amine and formaldehyde

The light solubilizable photosensitive components which can be used here include the following:

- (4) A component which contains a complex of a diazo compound with an inorganic salt or organic acid, or quinonediazo
- (5) Naphthoquinone 1,2-diazido-5-sulfonate of phenol or novolak resin, etc. obtained by combining a quinonediazo with a proper polymer binder

As the photosensitive component used in the present invention, any of the above can be used. As the photosensitive component which can be simply used as a mixture with inorganic fine grains, those stated in (1) are preferable.

A photosensitive monomer refers to a compound with a carbon-carbon unsaturated bond. The photosensitive monomers which can be used here include, for example, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-pentyl acrylate, allyl acrylate, benzyl acrylate, butoxyethyl acrylate, butoxy triethylene glycol acrylate, cyclohexyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, 2-ethylhexyl acrylate, glycerol acrylate, glycidyl acrylate, heptadecafluorodecyl acrylate, 2-hydroxyethyl acrylate, isobornyl acrylate, 2-hydroxypropyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, 2-methoxyethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene glycol acrylate,

octafluoropentyl acrylate, phenoxyethyl acrylate, stearyl acrylate, trifluoroethyl acrylate, allylated cyclohexyl diacrylate, 1,4-butanediol diacrylate, 1,3-butylene glycol diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol diacrylate, dipentaerythritol hexaacrylate, dipentaerythritol monohydroxypentaacrylate, ditrimethylolpropane tetraacrylate, glycerol diacrylate, methoxylated cyclohexyl diacrylate, neopentyl glycol diacrylate, propylene glycol diacrylate, polypropylene glycol diacrylate, triglycerol diacrylate, trimethylolpropane triacrylate, acrylamide, aminoethyl acrylate, phenyl acrylate, phenoxyethyl acrylate, benzyl acrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, bisphenol A diacrylate, diacrylate of bisphenol A - ethylene oxide addition product, diacrylate of bisphenol A - propylene oxide addition product, thiophenol acrylate, benzylmercaptane acrylate, monomers obtained by substituting the hydrogen atoms of these aromatic rings by 1 to 5 chlorine or bromine atoms, styrene, p-methylstyrene, o-methylstyrene, m-methylstyrene, chlorinated styrene, brominated styrene, α -methyl styrene, chlorinated α -methylstyrene, brominated α -methylstyrene, chloromethylstyrene, hydroxymethylstyrene, carboxymethylstyrene, vinyl naphthalene, vinyl anthracene, vinyl carbazole, compounds obtained by substituting the

acrylate in the molecule of each of the above compounds partially or wholly by methacrylate, γ -methacryloxypropyltrimethoxysilane, 1-vinyl-2-pyrrolidone, etc. One or more of these compounds can be used in the present invention.

In addition to the above, the developability after photosensitization can be improved by adding an unsaturated acid such as an unsaturated carboxylic acid. The unsaturated carboxylic acids which can be used here include, for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinylacetic acid, their anhydrides, etc.

The binders which can be used here include polyvinyl alcohol, polyvinyl butyral, methacrylate polymers, acrylate polymers, acrylate-methacrylate copolymers, α -methylstyrene polymer, butyl methacrylate resin, etc.

Furthermore, oligomers and polymers obtained by polymerizing at least one of the above mentioned compounds with a carbon-carbon double bond can also be used. For polymerization, 10 wt% or more, preferably 35 wt% or more of any of these monomers and another photosensitive monomer can be copolymerized.

As the monomer to be copolymerized, if an unsaturated acid such as an unsaturated carboxylic acid is copolymerized, the developability after sensitizing can be further improved. The

unsaturated carboxylic acids which can be used here include, for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinylacetic acid, anhydrides of these acids, etc.

It is preferable that the acid value (AV) of the polymer or oligomer with acidic groups such as carboxyl groups in the side chains obtained like this is 50 to 180. A more preferable range is 70 to 140. If the acid value is less than 50, the development allowable range becomes narrow. If the acid value exceeds 180, the solubility of non-exposed portions in the developer declines, and so if the developer concentration is raised, the exposed portions, too, peel, making it hard to obtain a highly precise pattern.

If photo-reactive groups are added to the side chains or molecular ends of the above polymer or oligomer, it can be used as a photosensitive polymer or photosensitive oligomer.

Preferable photo-reactive groups are ethylenic unsaturated groups which include vinyl groups, allyl groups, acryl groups, methacryl groups, etc.

Such side chains can be added to an oligomer or polymer, by letting an ethylenic unsaturated compound with a glycidyl group or isocyanato group or acrylic acid chloride, methacrylic acid chloride or allyl chloride addition-react with the mercapto groups, amino groups, hydroxyl groups or carboxyl groups in the polymer.

The ethylenic unsaturated compounds with a glycidyl group which can be used here include glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, glycidyl ethylacrylate, crotonyl glycidyl ether, glycidyl crotonate ether, glycidyl isocrotonate ether, etc.

The ethylenic unsaturated compounds with an isocyanato group which can be used here include (meth)acryloyl isocyanate, (meth)acryloylethyl isocyanate, etc.

It is preferable to add an ethylenic unsaturated compound with a glycidyl group or isocyanate, acrylic acid chloride, methacrylic acid chloride or allyl chloride by 0.05 to 1 mole equivalent for each mole equivalent of the mercapto groups, amino groups, hydroxyl groups or carboxyl groups in the polymer.

The photo polymerization initiators which can be used here include, for example, benzophenone, methyl o-benzoylbenzoate, 4,4-bis(dimethylamine)benzophenone, 4,4-bis(diethylamino)benzophenone, 4,4-dichlorobenzophenone, 4-benzoyl-4-methyl diphenyl ketone, dibenzyl ketone, fluorenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenyl-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone, p-t-butylldichloroacetophenone, thioxanthone, 2-methylthioxanthone, 2-chlorothioxanthone, 2-isopropylthioxanthone, diethylthioxanthone, benzyl, benzylldimethyl ketanol, benzylmethoxyethyl acetal, benzoin, benzoin methyl ether, benzoin butyl ether, anthraquinone,

2-t-butylanthraquinone, 2-amylanthraquinone, γ -chloroanthraquinone, anthrone, benzanthrone, dibenzosuberone, methyleneanthrone, 4-azidobenzalacetophenone, 2,6-bis(p-azidobenzylidene)cyclohexanone, 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone, 2-phenyl-1,2-butadione-2-(o-methoxycarbonyl)oxime, 1-phenylpropanedione-2-(o-ethoxycarbonyl)oxime, 1,3-diphenylpropanetrione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-3-ethoxypropanetrione-2-(o-benzoyl)oxime, Michler's ketone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propanone, naphthalenesulfonyl chloride, quinolinesulfonyl chloride, N-phenylthioacridone, 4,4'-azobisisobutyronitrile, diphenyl disulfide, benzthiazole disulfide, triphenylphosphine, camphorquinone, carbon tetrabromide, tribromophenylsulfone, benzoyl peroxide and combinations consisting of a photoreducing dye such as Eosine or Ethylene Blue and a reducing agent such as ascorbic acid or triethanolamine. In the present invention, one or more of them can be used.

The photopolymerization initiator is added by 0.1 to 6 wt% based on the weight of the photosensitive component. A more preferable range is 0.2 to 5 wt%. If the amount of the polymerization initiator is too small, the sensitivity to light becomes low, and if too large, more exposed portions may remain.

It is also effective to add an ultraviolet light absorber. If an absorber high in ultraviolet light absorbing effect is

added, a high aspect ratio, high preciseness and high resolution can be obtained. As the ultraviolet light absorber, an organic dye can be used. Above all, it is preferable to use an organic dye with a high UV absorption coefficient in a wavelength range of 350 to 450 nm. The organic dyes which can be used here include azo dyes, aminoketone dyes, xanthene dyes, quinoline dyes, aminoketone dyes, anthraquinone dyes, benzophenone dyes, diphenylcyanoacrylate dyes, triazine dyes, p-aminobenzoic acid dyes, etc. An organic dye is preferable since it does not remain in the burned insulation film even if it is added as a light absorber and since the decline of the insulation film properties by the light absorber can be decreased. Among the organic dyes, especially azo dyes and benzophenone dyes are preferable. It is preferable that the amount of the organic dye added is 0.05 to 5 wt%. If the amount of the organic dye is less than 0.05 wt%, the effect of adding an ultraviolet light absorber decreases, and if more than 5 wt%, the properties of the burned insulation film decline unpreferably. A more preferable range is 0.15 to 1 wt%. An ultraviolet light absorber comprising an organic dye can be added, for example, by preparing a solution with an organic dye dissolved in an organic solvent, mixing a glass powder into the organic solvent, and drying. According to this method, capsules with the surfaces of individual grains of the glass powder coated with an organic film can be produced.

A sensitizer is added to improve the sensitivity. The sensitizers which can be used here include, for example, 2,4-diethylthioxanthone, isopropylthioxanthone, 2,3-bis(4-diethylaminobenzal)cyclopentanone, 2,6-bis(4-dimethylaminobenzal)cyclohexanone, 2,6-bis(4-dimethylaminobenzal)-4-methylcyclohexanone, Michler's ketone, 4,4-bis(diethylamino)-benzophenone, 4,4-bis(diethylamino)chalcone, 4,4-bis(diethylamino)chalcone, p-dimethylaminocinnamylideneindanone, p-dimethylaminobenzylideneindanone, 2-(p-dimethylaminophenylvinylene)-isonaphthothiazole, 1,3-bis(4-dimethylaminobenzal)acetone, 1,3-carbonyl-bis(4-diethylaminobenzal)acetone, 3,3-carbonyl-bis(7-diethylaminocoumarin), N-phenyl-N-ethylethanolamine, N-phenylethanolamine, N-tolyldiethanolamine, N-phenylethanolamine, isoamyl dimethylaminobenzoate, isoamyl diethylaminobenzoate, 3-phenyl-5-benzoylthiotetrazole, 1-phenyl-5-ethoxycarbonylthiotetrazole, etc. In the present invention, one or more of them can be used. Among sensitizers, some can be used also as photo polymerization initiators. When a sensitizer is added to the photosensitive paste of the present invention, the amount is usually 0.05 to 10 wt% based on the amount of the photosensitive component. A preferable range is 0.1 to 10 wt%. If the amount of the sensitizer is too small, the effect of improving the photosensitivity cannot be

manifested, and if too large, the exposed portion remaining rate may become too small.

A photosensitive fluorescent paste is usually produced by mixing a fluorescent powder, ultraviolet light absorber, photosensitive polymer, photosensitive monomer, photo polymerization initiator and solvent at a predetermined ratio, and homogeneously mixing and dispersing the mixture by a three-roller mill or kneading machine.

The viscosity of the paste can be properly adjusted by adjusting the mixing ratio of the fluorescent powder, organic solvent, plasticizer, precipitation preventive, etc. A preferable viscosity range is 0.1 to 100 P (poises), and a more preferable range is 0.1 to 20 P.

The glass substrate used in the present invention is not especially limited, and a general soda lime glass or a glass obtained by annealing a soda lime glass, or a glass with a high strain point (e.g., "PD-200" produced by Asahi Glass Co., Ltd.), etc. can be used. The size of the glass substrate is not especially limited, and a 1 to 5 mm thick glass can be used.

By forming fluorescent material layers on a glass substrate with electrodes and partitions formed on it, a board for a plasma display can be obtained. A substrate with a dielectric layer formed on it in addition to electrodes and partitions can also be used. The electrodes can be formed by applying silver, aluminum, copper, gold, nickel, tin oxide or

ITO, etc. by screen printing or using a photosensitive conductive paste.

The partitions can be formed like a grid or in stripes, but in the present invention, partitions formed in stripes are especially effective. It is preferable that the pitch of the partitions is 80 to 500 μm . A more effective pitch is 80 to 200 μm . That is, when highly precise partitions are formed, the present invention is effective.

It is preferable to use a glass with a thermosoftening point of 300 to 600°C as the partitions. As the material of the glass, it is preferable to use a glass with a refractive index of 1.5 to 1.7 to allow highly precise processing according to the photolithography.

Examples of forming the fluorescent material layers of the plasma display according to the present invention are described below, but the present invention is not limited thereto or thereby.

(1) Coating step

A glass substrate with an electrode layer and a partition layer formed on it is coated with fluorescent pastes at desired places. For coating, each of the fluorescent pastes is discharged from a paste applicator with one or more outlet holes. The fluorescent pastes of R, G and B colors are applied in stripes by turns, to form fluorescent material layers of respective colors.

So, it is preferable to discharge a fluorescent paste from a paste applicator with 1 to 2000 outlet holes, and to repeat this operation for R, G and B, i.e., three times in total. As another method, the fluorescent materials of respective R, G and B colors can also be discharged simultaneously from a paste applicator designed to allow simultaneous discharge of R, G and B fluorescent materials.

Each of the fluorescent materials of a plasma display is required to have a thickness of 10 to 50 μm on the bottoms of the spaces between the respectively adjacent partitions and along the lateral sides (as a thickness measured at a half-height position of each partition) of the partitions.

Considering the shrinkage due to drying and burning, it is preferable to apply with a thickness of about 20 to 80 μm .

(2) Drying step

The coating is followed by drying. If the coated substrate is dried with the coated side turned downward, the fluorescent material layers of the respective colors can be formed uniformly on the bottoms of the spaces between the respectively adjacent partitions and along the lateral sides. The angle of the substrate with the coated side turned downward is 0 to 30 degrees as an angle formed between the glass substrate and the horizontal plane. The drying temperature and time depend on the paste compositions and viscosities, but it is preferable to dry at 50 to 200°C for 5 to 60 minutes.

(3) Exposure step

If photosensitive fluorescent pastes are used, exposure and development are necessary. For exposure, generally mask exposure using a photomask is effected as in ordinary photolithography. Either a negative or positive mask is selected, depending on the photosensitive organic component used. As another method, a laser beam, etc. can also be used for direct drawing without using any photomask. As the exposure machine, a stepper exposure machine or proximity exposure machine, etc. can be used.

For exposing a large area, after the substrate such as a glass substrate has been coated with photosensitive pastes, the substrate can be carried forward during exposure, to expose a large area by an exposure machine with a small effective exposure area.

The active light used in this case can be visible light, near ultraviolet light, ultraviolet light, electron beam, X ray or laser beam, etc. Among them, ultraviolet light is preferable. The light source can be, for example, a low pressure mercury lamp, high pressure mercury lamp, extra-high pressure mercury lamp, halogen lamp or germicidal lamp, etc. Among them, an extra-high pressure mercury lamp is suitable.

If a photomask is used, the design of the pattern width is important. Usually, a width equal to the space obtained by subtracting the partition width from the partition pitch is used,

but considering the accuracy of alignment and the light scattering at the time of exposure, a photomask with a pattern width more narrow than the space by 0 to 30 mm can also be used.

(4) Development step

After completion of exposure, a developer is used for development. In this case, immersion, spray or brushing is used.

The developer can be an organic solvent which allows the organic component in the photosensitive pastes to be dissolved. The organic solvent can also contain water to such an extent that the dissolving power may not be lost. If a compound with an acidic group such as a carboxyl group exists in the photosensitive paste, an alkali aqueous solution can be used for development. The alkali aqueous solution can be an alkali metal aqueous solution such as sodium hydroxide or calcium hydroxide aqueous solution, but the use of an organic alkali aqueous solution is preferable since the alkali component can be easily removed at the time of burning.

The organic alkali can be an amine compound. The organic alkalis which can be used here include tetramethylammonium hydroxide, trimethylbenzylammonium hydroxide, monoethanolamine, diethanolamine, etc. The concentration of the alkali aqueous solution is usually 0.01 to 10 wt%, preferably 0.1 to 5 wt%. If the alkali concentration is too low, the non-exposed portions cannot be removed, and if too high,

the pattern may peel to erode the exposed portions. In view of process control, it is preferable that the development temperature is 20 to 50°C.

(5) Burning step

The development is followed by burning in a burning furnace. The burning atmosphere and temperature depend on the pastes and substrate used. The burning is effected in an atmosphere of air, nitrogen or hydrogen, etc. The burning temperature is 400 to 610°C. The burning furnace used can be a batch burning furnace or a belt type or roller-hearth type continuous burning furnace.

In addition to the above steps, a heating step of 50 to 300°C can also be used for drying or preliminary reaction.

The glass substrate with the fluorescent material layers of the respective colors obtained through the above steps can be used on the rear side of a plasma display. If the formed glass substrate is sealed with the glass substrates on the front and rear faces, and a rare gas such as helium, neon or xenon is introduced into the sealed housing, then the panel of a plasma display can be produced. Furthermore, if a driver IC is mounted, a plasma display can be produced.

[Examples]

The present invention is described below concretely in reference to examples, but is not limited thereto or thereby.

In the following examples, each concentration (%) is wt% unless otherwise stated.

Example 1

Fluorescent pastes respectively consisting of 50 g of a fluorescent powder, 40 g of a binder polymer (methyl methacrylate-methacrylic acid-styrene copolymer), 30 g of a solvent (γ -butyrolactone) and 4 g of a dispersing agent were prepared. The fluorescent powders used were red (Y, Gd, Eu)BO₃, green (Zn, Mn)₂SiO₄ and blue (Ba, Eu)MgAl₁₀O₁₇. At first the respective organic ingredients were dissolved by heating at 80°C, and then a fluorescent powder was added. The mixture was kneaded by a kneader, to prepare a paste. The respective pastes were adjusted to be 0.5 P in viscosity by adjusting the amount of the solvent.

A glass substrate with two thousand 120 μ m high 30 μ m wide partitions formed at a pitch of 150 μ m was coated with the respective pastes of red, green and blue in stripes.

For coating, from a paste applicator having 640 outlet holes with a diameter of 80 μ m formed at a pitch of 450 μ m, at first the red fluorescent paste was discharged, and dried at 80°C for 60 minutes with the coated side turned downward. Then, the blue fluorescent paste was discharged, and dried at 80°C for 60 minutes with the coated side turned downward. Subsequently, the blue fluorescent paste was discharged, and dried at 80°C for 60 minutes with the coated side turned downward.

Furthermore, the obtained glass substrate was burned at 500°C for 30 minutes.

The thicknesses of the layers formed along the lateral sides and on the bottoms of the spaces between the respectively adjacent partitions were observed by an electron microscope. It was found that the respective fluorescent materials were formed in stripes with a thickness of $20 \pm 5 \mu\text{m}$ on the lateral sides and with a thickness of $30 \pm 4 \mu\text{m}$ on the bottoms of the respective spaces.

Example 2

Fluorescent pastes respectively consisting of 50 g of a fluorescent powder, 40 g of a binder polymer (methyl methacrylate-methacrylic acid-styrene copolymer), 30 g of a solvent (γ -butyrolactone) and 4 g of a dispersing agent were prepared. The fluorescent powders used were red (Y, Gd, Eu)BO₃, green (Zn, Mn)₂SiO₄ and blue (Ba, Eu)MgAl₁₀O₁₇. At first the respective organic ingredients were dissolved by heating at 80°C, and then a fluorescent powder was added. The mixture was kneaded by a kneader, to prepare a paste. The respective pastes were adjusted to be 0.3 P in viscosity by adjusting the amount of the solvent.

A glass substrate with two thousand 140 μm high 50 μm wide partitions formed at a pitch of 360 μm was coated with the respective pastes of red, green and blue in stripes.

For coating, a paste applicator having 1940 outlet holes with a diameter of $100\text{ }\mu\text{m}$ formed at a pitch of $360\text{ }\mu\text{m}$ and designed to discharge the red fluorescent paste, the blue fluorescent paste and the green fluorescent paste respectively was used to discharge the respective fluorescent materials, and the respective fluorescent pastes were dried at 80°C for 45 minutes. Furthermore, the obtained glass substrate was burned at 500°C for 30 minutes.

The thicknesses of the respective fluorescent material layers along the lateral sides and on the bottoms of the spaces between the respectively adjacent partitions were observed by an electron microscope. It was found that the respective fluorescent materials were formed in stripes with a thickness of $10 \pm 5\text{ }\mu\text{m}$ along the lateral sides and with a thickness of $40 \pm 4\text{ }\mu\text{m}$ on the bottoms of the spaces.

Example 3

Fluorescent pastes respectively consisting of 50 g of a fluorescent powder, 20 g of a binder polymer (methyl methacrylate-methacrylic acid-styrene copolymer), 20 g of trimethylolpropane triacrylate, 30 g of a solvent (γ -butyrolactone), 4 g of a dispersing agent and a photopolymerization initiator ("Irgacure 907" produced by Ciba Geigy) were prepared. The fluorescent powders used were red (Y, Gd, Eu) BO_3 , green (Zn, Mn) $_2\text{SiO}_4$ and blue (Ba, Eu) $\text{MgAl}_{10}\text{O}_{17}$. At first the respective organic ingredients were dissolved by

heating at 80°C, and then a fluorescent powder was added. The mixture was kneaded by a kneader, to prepare a paste. The respective pastes were adjusted to be 0.3 P in viscosity by adjusting the amount of the solvent.

A glass substrate with two thousand 120 μm high 30 μm wide partitions formed at a pitch of 150 μm was coated with the respective pastes of red, green and blue in stripes.

For coating, a paste applicator having 640 outlet holes with a diameter of 80 μm formed at a pitch of 450 μm was used to discharge the red fluorescent paste, the green fluorescent paste and the blue fluorescent paste in this order, and the respective pastes were dried at 80°C for 60 minutes with the coated side turned downward. Then, a negative photomask with 60 μm wide lines formed at a pitch of 150 μm was aligned for exposure, and the exposed glass substrate was developed by 0.5% sodium carbonate aqueous solution and burned at 500°C for 30 minutes.

The thicknesses of the respective fluorescent material layers along the lateral sides and on the bottoms of the spaces between the respectively adjacent partitions were observed by an electron microscope. It was found that the respective fluorescent materials were formed in stripes with a thickness of 23 ± 2 μm along the lateral sides and with a thickness of 30 ± 6 μm on the bottoms of the spaces.

[Effects of the invention]

The present invention allows the fluorescent material layers of a plasma display to be simply and easily formed. Furthermore, fluorescent material layers suitable for a highly precise plasma display can be formed.

[Brief description of the drawings]

[Fig. 1] A drawing showing a fluorescent material layer coating method of the present invention.

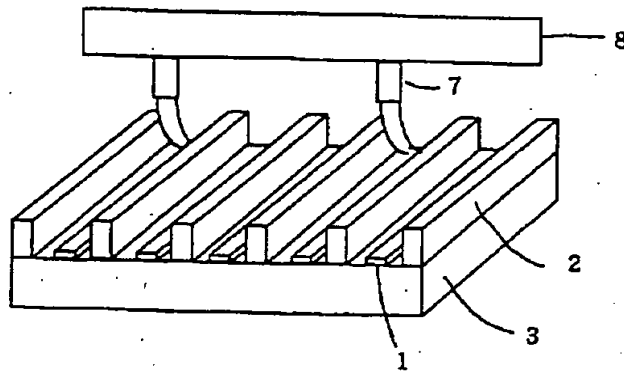
[Fig. 2] A drawing showing a plasma display panel after fluorescent material layer coating of the present invention.

[Fig. 3] A drawing showing a plasma display panel after burning of the present invention.

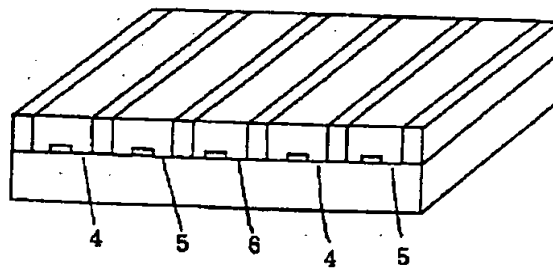
[Meanings of symbols]

- 1 ... electrode
- 2 ... partition
- 3 ... glass substrate
- 4 ... red fluorescent material layer
- 5 ... blue fluorescent material layer
- 6 ... green fluorescent material layer
- 7 ... outlet hole
- 8 ... paste applicator

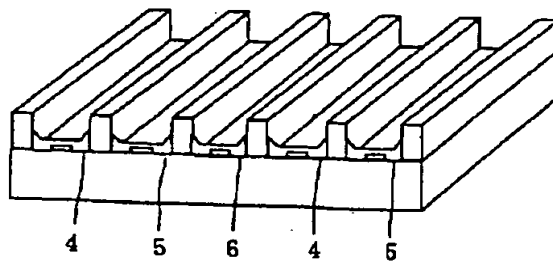
[Fig. 1]



[Fig. 2]



[Fig. 3]



[Title of the document] Abstract

[Abstract]

[Problem] To provide a method for producing a plasma display which allows simple formation of fluorescent material layers.

[Solving means] Fluorescent pastes respectively containing a fluorescent material and an organic binder are discharged from outlet holes, to form fluorescent material layers at desired places. The object can be achieved by a method for producing a plasma display, characterized in that the spaces A formed between the respectively adjacent partitions and the average diameter B of the outlet holes satisfy the following condition:

$$500 \mu\text{m} \geq A > B \geq 10 \mu\text{m}$$

[Selected drawing] Nil